

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 506 206 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(21) Application number: 92201346.1

(51) Int. Cl.<sup>5</sup>: B01J 37/20, C10G 45/08

(22) Date of filing: 21.04.88

This application was filed on 12 - 05 - 1992 as a  
divisional application to the application  
mentioned under INID code 60.

(30) Priority: 22.04.87 JP 99313/87  
12.06.87 JP 145141/87  
12.06.87 JP 145142/87  
12.06.87 JP 145143/87  
12.06.87 JP 145144/87

(43) Date of publication of application:  
30.09.92 Bulletin 92/40

(60) Publication number of the earlier application in  
accordance with Art.76 EPC: 0 289 211

(84) Designated Contracting States:  
DE FR GB NL

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(54) A catalyst for hydrotreating hydrocarbons and methods of activating the same.

(57) New supported catalysts for hydrotreating hydrocarbons comprise (a) at least one member selected from the group consisting of oxides of metals in the Periodic Table's Groups VI and VIII, and (b) at least one organic compound having a mercapto radical or radicals (-SH) selected from bivalent mercaptans, amino-substituted mercaptans, and thiocarboxylic acids. These new catalysts can be easily activated by treatment in the presence of hydrogen gas at a temperature in the range from room temperature to 400°C, showing higher activity than those activated by conventional methods.

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This invention relates to a catalyst for hydrotreating hydrocarbon oil that can be easily activated, and to a method of activating the same.

For the so-called hydrotreatment process (treatment of hydrocarbon oil in the presence of hydrogen to effect hydrogenation, hydrodesulphurization, hydrodenitrification and hydrogenolysis), have been used those catalysts which comprise, as active ingredient, at least one member selected from the group consisting of the metals in the Periodic Table's Groups VI and VIII and are supported on an inorganic oxide carrier, such as alumina, silica-alumina and titania. Molybdenum and tungsten are frequently used as the Group VI metal, and cobalt and nickel are often employed as the Group VIII metal.

These metals, usually supported on a carrier in the form of inactive oxide, must be activated before use by presulphiding for conversion from the oxide to sulphide form.

This presulphiding is generally effected by charging the catalyst to be activated in a reactor for hydrotreatment of hydrocarbon oil and passing a sulphurizing agent together with hydrogen gas through the catalyst bed. The conditions of this presulphiding vary with the type of intended hydrotreatment process and the kind of sulphurizing agent used. When hydrogen sulphide is employed as the sulphurizing agent, it is diluted with hydrogen gas to a concentration of about 0.5 to 5 volume % and the resulting gaseous mixture is passed at a temperature higher than 180 °C (usually higher than 250 °C) in an amount of 1000 to 3000 litres (at standard temperature and pressure) for 1 litre of catalyst. When carbon disulphide, n-butylmercaptan, dimethyl sulphide or dimethyl disulphide is used, it is diluted before use with light hydrocarbon oil and sulphurization is carried out at a temperature of 250 to 350 °C, under a pressure of 20 to 100 Kg/cm<sup>2</sup>, at a liquid space velocity of 0.5 to 2 hr<sup>-1</sup> and with a hydrogen/oil ratio of 200 to 1000 Nl/l. After finishing this presulphiding of catalyst, feedstock to be treated is fed to the reactor to start the hydrotreatment process.

This presulphiding step, on which successful operation of the succeeding hydrotreatment process depends, must be performed with great care by using proper materials. When a diluent is used, for example, a hydro-carbon oil containing no olefin must be selected, as otherwise the catalyst is poisoned by the polymeric substances formed from the olefins contained. In addition, heavy oil is unsuitable as the diluent because of its poor wetting on catalyst surface due to the high viscosity. As a result, light hydrocarbon oil has to be used as the diluent, leading to an increase in production cost. Furthermore, the sulphurizing agent must be used in a relatively large amount to prevent the catalyst reduction from being inactivated by the reaction with hydrogen at high temperatures, and hence the weight ratio of sulphurizing agent to hydrogen must be maintained at a proper level throughout the presulphiding process. This preliminary step is rarely automated, and requires unusual and cumbersome operations, imposing a heavy burden on the operators. Thus, how to eliminate this presulphiding step, or how to minimize the cumbersome operations involved, has been a subject of major concern.

A method to meet this demand was recently proposed, which comprises impregnating a supported catalyst of an active metal with a polysulphide represented by the general formula of R-S<sub>n</sub>-R' (wherein n is an integer of 3 to 20, and R and R' are each hydrogen atom or an organic group of 1 to 150 carbon atoms), and heat-treating the polysulphide-impregnated catalyst in the absence of hydrogen gas at a temperature of 65 to 275 °C and under a pressure of 0.5 to 70 bar [Japanese Patent Kokai No. 111144 (1986)]. This method, in which the active metal is sulphurized by the polysulphide contained in the catalyst upon heating, eliminates the use of any sulphurizing agent and a diluent therefor when presulphiding is allowed to proceed inside the reactor, thus simplifying the operation. This method also makes it possible to effect presulphiding outside the reactor and to start hydrotreatment process immediately after the sulphurized catalyst is charged in the reactor. However, the polysulphide has to be used in the form of a solution in an organic solvent for impregnation, and hence a special contrivance is needed for the use of organic solvents in carrying out the impregnation process.

#### SUMMARY OF THE INVENTION

The object of this invention is to eliminate the aforementioned problems associated with the conventional catalyst, and to provide a new catalyst for hydrotreating hydrocarbon oil that can be easily sulphurized for activation and a method of activating the same.

Comprehensive studies to seek for new sulphurizing agents easier to handle than the above-mentioned poly-sulphides have led us to find that organic compounds having mercapto radical (-SH) are best suited for the purpose. This invention was accomplished based on these findings.

Thus, the first aspect of this invention relates to a catalyst for hydrotreating hydrocarbons supported on an inorganic oxide carrier, which comprises (a) at least one member selected from the group consisting of oxides of metals in the Periodic Table's Groups VI and VIII, and (b) at least one organic compound having a

mercapto radical or radicals (-SH) selected from bivalent mercaptans represented by the general formula, HS-R'-SH (wherein R' is a bivalent hydrocarbonaceous radical); amino-substituted mercaptans represented by the general formula, H<sub>2</sub>N-R'-SH (wherein R' is as defined above); and thiocarboxylic acids represented by the general formula, R''-COSH (wherein R'' is a monovalent hydrocarbonaceous radical). The second aspect of this invention relates to a method of activating the catalyst as defined above which comprises treating it in the presence of hydrogen gas at a temperature in the range from room temperature to 400 °C.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

As is well known, alumina, silica-alumina, titania and others are used as the inorganic oxide carrier for catalysts of this type. Of these, alumina and silica-alumina are the most typical examples.

It is also known that molybdenum and/or tungsten are preferable as the active metal of Group VI, and cobalt and/or nickel are preferred examples of the active metal of Group VIII. The oxides of these metals may be used either alone or in combination.

The catalyst of this invention may also contain, as active component, oxide of phosphorus in addition to oxides of Group VI and Group VIII metals. Phosphorus may be deposited on the carrier either separately or simultaneously with the active metals. In the latter case in which a solution containing all the active components is used for impregnation, the largest possible amount of phosphorus that can be included in the catalyst is 8 weight % as P<sub>2</sub>O<sub>5</sub> because the treating solution becomes more viscous as its phosphorus content increases, making impregnation increasingly less effective.

As preferable examples of the sulphurizing agents, there may be mentioned the following compounds: bivalent mercaptans represented by the general formula, HS-R'-SH (wherein R' is a bivalent hydrocarbonaceous radical), such as ethanedithiol (HSCH<sub>2</sub>CH<sub>2</sub>SH) and 1,4-butanedithiol (HS(CH<sub>2</sub>)<sub>4</sub>SH); amino-substituted mercaptans represented by the general formula, H<sub>2</sub>N-R'-SH (wherein R' is as defined above), such as 2-aminoethanethiol (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>SH) and 4-aminothiophenol (HNCH<sub>4</sub>SH); and thiocarboxylic acids represented by the general formula, R''-COSH (wherein R'' is a monovalent hydrocarbonaceous radical), such as thioacetic acid (CH<sub>3</sub>COSH) and thiobenzoic acid (C<sub>6</sub>H<sub>5</sub>COSH).

A solution of the above-mentioned sulphurizing agent is soaked by impregnation into an inorganic carrier bearing at least one member selected from the metals in the Periodic Table's Groups VI and VIII. In this case, use of an aqueous solution is most advantageous in terms of cost.

The preferable amount of sulphurizing agent to be included is 1 to 3 equivalent proportions based on the weight required for converting the Group VI and/or VIII metals to a sulphurized state highly active for hydrogenation (for example, MoS<sub>2</sub>, WS<sub>2</sub>, CoS and NiS). A smaller amount results in lower catalytic activity, while use of a larger amount is uneconomical because no marked enhancement of activity cannot be expected.

Some catalysts soaked with a solution of sulphurizing agent show activity without any further treatment; in other cases, however, activity can be exhibited by removing the solvent used for dissolving the sulphurizing agent, followed by treatment in the presence of hydrogen gas at a temperature in the range from room temperature to 400 °C (the solvent removal may be performed during the activation step in the presence of hydrogen gas).

During the activation step in the presence of hydrogen gas, the sulphurizing agent attached to the active metal through coordinate bond undergoes hydrogenolysis, converting the metal component into sulphided form which is an active species for hydrogenation. In effecting this activation process, there is no specific limitation upon the reaction pressure, and presence of hydrocarbons in the reaction system causes no problem. Hence, this step may be carried out in the reactor used for hydrocarbon hydrotreatment or in a separate activation apparatus.

Activation is conducted at a temperature in the range from room temperature to 400 °C, preferably in the range from 100 to 300 °C. A treating temperature higher than 400 °C results in lowered catalytic activity.

The catalysts prepared by the method of this invention show higher activity in hydrodesulphurization of hydrocarbon oil than those sulphurized by the conventional method. The reason is not absolutely clear yet, but it may be assumed that the sulphurizing agent used herein is attached to the Group VI and/or VIII metal through coordinate bond and this is effective in forming the metal sulphides favourable in the succeeding activation step.

The following Examples and Comparative Examples will further illustrate the invention.

#### EXAMPLE 1

Twenty grams of a commercial catalyst containing 15 weight % of MoO<sub>3</sub> and 4 weight % of CoO

supported on  $\gamma$ -alumina (KF-742; product of Nippon Ketjen Co Ltd) was thoroughly impregnated with 12 ml of an aqueous solution containing 6.0 g mercaptoacetic acid ( $d^{20}_4$ : 1.33) and dried at 30 °C for 16 hours, giving catalyst A<sub>1</sub>. Catalysts A<sub>2</sub> and A<sub>3</sub> were prepared in much the same manner as above, except that 9.0 g and 12.0 g of mercaptoacetic acid were used, respectively. Catalyst A<sub>4</sub> was prepared by impregnating 20 g of the commercial catalyst (KF-742) with 12 ml of an aqueous solution containing 7.5 g mercaptoacetic acid, drying at 80 °C for 16 hours, and repeating the impregnation and drying steps once again.

The amounts of mercaptoacetic acid loaded on catalysts A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> and A<sub>4</sub> were respectively 1.2, 1.8, 2.4 and 3.0 times the theoretical amount required to convert the two metals into MoS<sub>2</sub> and CoS.

Separately, 500 g of an alumina carrier (specific surface area: 310 m<sup>2</sup>/g; pore volume: 0.70 ml/g) used in KF-742 was impregnated with a solution prepared from 111 g ammonium paramolybdate, 101 nickel nitrate hexahydrate 150 g conc. ammonia water, dried at 110 °C for 16 hours and calcined at 500 °C for two hours, giving a catalyst containing 15 weight % of MoO<sub>3</sub> and 4 weight % of NiO. This base catalyst was then treated in the same manner as above to include varying amounts of mercaptoacetic acid, affording catalysts A<sub>5</sub>, A<sub>6</sub>, A<sub>7</sub> and A<sub>8</sub>:

The amounts of mercaptoacetic acid loaded on catalysts A<sub>5</sub>, A<sub>6</sub>, A<sub>7</sub> and A<sub>8</sub> were respectively 1.2, 1.8, 2.4 and 3.0 times the theoretical amount required to convert the two metals into MoS<sub>2</sub> and NiS.

In addition, 20 g of the commercial catalyst (KF-742) was thoroughly impregnated with 12 ml of an aqueous solution containing 10.0 g mercaptopropionic acid ( $d^{20}_4$ : 1.22) and dried at 80 °C for 16 hours, giving catalyst A<sub>9</sub>.

The amount of mercaptopropionic acid included in this catalyst was 1.8 times the theoretical amount required to convert the two metals into MoS<sub>2</sub> and CoS.

#### (Activation)

Three millilitres each of the catalysts prepared above (A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, A<sub>4</sub>, A<sub>5</sub>, A<sub>6</sub>, A<sub>7</sub> and A<sub>8</sub>) was charged in a fixed-bed flow reactor made of stainless steel and activated under the conditions shown below.

Amount of catalyst	3 ml
Pressure	Atmospheric pressure
Hydrogen flow rate	4.8 Nl/hr
Reaction time	3 hours
Reaction temperature	200 °C

(Activity evaluation)

The catalysts thus activated were used for hydrodesulphurization of straight-run gas oil distilled from Kuwait crude oil: hereinafter abbreviated as KSRGO. For catalyst A<sub>2</sub>, the substance not subjected to the activation process (referred to as catalyst A'<sub>2</sub>) was also tested in the same way as above. The properties of the KSRGO used for the reaction were:

Specific gravity (15/4 °C)	0.848
Sulphur (% by weight)	1.61 ✓
Nitrogen (ppm by weight)	157 ✓
Initial boiling point (°C)	211 ✓
50 vol-% boiling point (°C)	340 ✓
Final boiling point (°C)	406 ✓

The reaction was conducted under the conditions shown below using a fixed-bed reactor.

Amount of catalyst	3 ml	✓
Liquid space velocity of feed oil	2.0 hr <sup>-1</sup>	✓
Pressure (hydrogen pressure)	30 kg/cm <sup>2</sup>	✓
Reaction temperature	330 °C	✓
Hydrogen/oil ratio	300 N1/1	✓
Reaction time	8 hours	✓

Hydrotreated oil samples were taken from reactor at an interval of two hours for determination of sulphur content. The average desulphurizing rate obtained from the oil analysis for 4 hours, 6 hours and 8 hours after the start of reaction is shown in Table 1.

#### COMPARATIVE EXAMPLE 1

The catalysts of MoO<sub>3</sub>/CoO and MoO<sub>3</sub>/NiO types (hereinafter abbreviated as Mo/Co and Mo/Ni types) used in Example 1 and 2 were subjected to presulphiding using n-butylmercaptan diluted with KSRGO, and tested for hydrosulphurization activity.

(Sulphurizing treatment)

Sulphurizing agent	3 wt % n butylmercaptan in KSRGO
Amount of catalyst	3 ml
Liquid space velocity of feed oil	2.0 hr <sup>-1</sup>
Reaction pressure	30 kg/cm <sup>2</sup>
Reaction temperature	316 °C
Hydrogen/oil ratio	300 N1/1
Reaction time	8 hours

(Activity evaluation)

Catalytic activity was evaluated under the same conditions as in Example 1. The average desulphurization rate for 4 hours, samples taken 4 hours, 6 hours and 8 hours after the start of reaction is shown in Table 1.

For both of the Mo/Co and Mo/Ni types, catalysts containing mercaptoacetic acid or mercaptopropionic acid showed higher activity than those sulphurized with a mixture of 3 weight % n-butylmercaptan and KSRGO. With the catalysts of Mo/Co type, addition of mercaptoacetic acid in an amount of 1.2 times the theoretical weight required to convert the two metals into MoS<sub>2</sub> and CoS suffices, with no marked enhancement of activity being observed with a larger amount. Catalyst A<sub>2</sub> was slightly lower in activity than catalyst A<sub>1</sub>, but showed higher activity than catalysts sulphurized with n-butylmercaptan by the conventional method. With the catalysts of Mo/Ni type, on the other hand, the optimum amount of mercaptoacetic acid to be added was somewhat larger than with catalysts of Mo/Co type, but did not exceed a level of 1.5 times the theoretical weight.

#### RESULTS OF ACTIVITY EVALUATION USING KSRGO

Table 1-(1)

(Mo/Co type)						
Catalyst	A <sub>1</sub>	A <sub>2</sub>	A' <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	Sulphurized with n-BM(*)
Content of mercaptoacetic acid (°)	x1.2	x1.8	x1.8	x2.4	x3.0	
Rate of desulphurization (%)	88.2	87.5	86.7	87.3	87.3	82.7

(\*)Sulphurized with 3 wt % n-butylmercaptan in KSRGO.

(\*) Factor based on the theoretical weight required for conversion into MoS<sub>2</sub>, CoS and NiS.

Table 1-(2)

(Mo/Ni type)					
Catalyst	A <sub>5</sub>	A <sub>6</sub>	A <sub>7</sub>	A <sub>8</sub>	Sulphurized with n-EM(*)
Content of mercaptoacetic acid (°)	x1.2	x1.3	x2.4	x3.0	-
Rate of desulphurization (%)	31.2	34.2	33.9	83.9	79.1

(\*)Sulphurized with 3 wt % n-butylmercaptan in KSRGO.

(\*) Factor based on the theoretical weight required for conversion into MoS<sub>2</sub>, CoS and NiS.

Table 1-(3)

(Mo/Co type)		
Catalyst	Ag	Sulphurized
Content of mercaptopropionic acid (°)	x1.3	-
Rate of desulphurization (%)	87.5	32.7

(\*) Factor based on the theoretical weight required for conversion into MoS<sub>2</sub>, CoS and NiS.

[The same applies to the subsequent tables for (°) and (°).]

**Example 2**

One hundred grams of  $\gamma$ -alumina carrier (specific surface area: 280 m<sup>2</sup>/g; pore volume: 0.75 ml/g) was impregnated with 80 ml of an aqueous solution prepared from 29.0 g molybdenum trioxide, 10.5 g nickel carbonate (Ni content: 43.3%), 16.5 g of 85% phosphoric acid and water, dried at 110 °C for 16 hours and calcined at 500°C for two hours, giving a catalyst containing 20 weight % of MoO<sub>3</sub>, 4 weight % of NiO and 7 weight % of P<sub>2</sub>O<sub>5</sub>. This base catalyst (20 g) was thoroughly impregnated with 10 ml of an aqueous solution containing 7.3 g mercaptoacetic acid and dried at 100 °C for 16 hours, affording catalyst B<sub>1</sub>.

Catalysts B<sub>2</sub> and B<sub>3</sub> were prepared in much the same manner as above, except that 11.0 g and 14.6 g of 100% mercaptoacetic acid were used, respectively, in place of the aqueous solution.

The amounts of mercaptoacetic acid loaded on catalysts B<sub>1</sub>, B<sub>2</sub> and B<sub>3</sub> were respectively 1.0, 1.5 and 2.0 times the theoretical amount required to convert the two metals into MoS<sub>2</sub> and NiS.

Separately, 20 g of the calcined catalyst prepared above was thoroughly impregnated with an aqueous solution containing 11.7 g mercaptopropionic acid and dried at 100 °C for 16 hours, giving catalyst B<sub>4</sub>. The amount of mercaptopropionic acid loaded on this catalyst was 1.5 times the theoretical amount required to convert the two metals into MoS<sub>2</sub> and NiS.

(Activity evaluation)

Catalysts B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub> and B<sub>4</sub> were used for hydrodesulphurization of KSRGO without being activated

under the same conditions as in Example 1. The average desulphurization rates are shown in Table 2.

### Comparative Example 2

- 5 The base catalyst of  $\text{MoO}_3/\text{NiO}/\text{P}_2\text{O}_5$  type (hereinafter abbreviated as Mo/Ni/P type) used in Example 2 was sulphurized in the same manner as in Comparative Example 2, and used for hydrodesulphurization of KSRGO in the same way as in Example 1. The average desulphurization rate is also shown in Table 2.

Table 2

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Results of Activity Evaluation Using KSRGO					
Catalyst	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>4</sub>	Sulphurized with n-BM(%)
	HSCH <sub>2</sub> COOH			HSCH <sub>2</sub> CH <sub>2</sub> COOH	
Content of sulphurizing agent (%)	x1.0	x1.5	x2.0	x1.5	-
Rate of desulphurization (%)	89.6	93.5	93.0	93.4	73.5

- 20 The catalyst containing mercaptoacetic acid or mercaptopropionic acid showed higher activity than the catalyst sulphurized with a mixture of 3 weight % n-butylmercaptan and KSRGO. Data of the catalyst containing mercaptoacetic acid indicate that addition of the acid in an amount of 1.5 times the theoretical weight required to convert the two metals into  $\text{MoS}_2$ ,  $\text{NiS}$  and  $\text{CoS}$  suffices, with no marked enhancement of activity being observed with larger amounts. Excessively large amounts of sulphurizing agent included in a catalyst not only results in its waste, but also requires two or more steps for impregnation.

### Example 3

- 30 Thirty grams of commercial catalyst containing 17 wt% of  $\text{MoO}_3$  and 4 wt% of  $\text{CoO}$  supported on  $\gamma$ -alumina (KF-707: product of Nippon Ketjen Co Ltd) was impregnated with 15 ml of ethanolic solution containing 7.9 g ethanedithiol or 10.2 g 1,4-butanedithiol, and dried at 80°C for 16 hours, giving catalysts E<sub>1</sub> and E<sub>2</sub>, respectively.

The amounts of dithiol loaded on these catalysts were 1.8 times the theoretical amount required to convert the two metals into  $\text{MoS}_2$  and  $\text{CoS}$ .

- 35 Catalysts E<sub>1</sub> and E<sub>2</sub> prepared above were activated in the same manner as in Example 1 and used for hydrodesulphurization of KSRGO under the same conditions. The average rates of desulphurization are shown in Table 5.

### Comparative Example 3

- 40 The base catalyst of Mo/Co type used in Example 3 was sulphurized in the same manner as in Comparative Example 2 and used for hydrodesulphurization of KSRGO in the same way as in Example 1. The rate of desulphurization is also shown in Table 5.

Table 5

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Catalyst	E <sub>1</sub>	E <sub>2</sub>	Sulphurized with n-BM(%)
Bivalent mercaptan	Ethanedithiol	1,4-butanedithiol	-
Amount (%)	x1.8	x1.8	
Rate of desulphurization (%)	90.1	86.9	81.5

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The catalysts of Mo/Co type containing ethanedithiol or 1,4-butanedithiol showed higher activity than the catalyst sulphurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

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### Example 4

One hundred grams of  $\gamma$ -alumina carrier (the same type as used in Example 2) was impregnated with

80 ml of a solution prepared from 29.0 g molybdenum trioxide, 10.5 g nickel carbonate (Ni content: 43.3%), 16.5 g of 85% phosphoric acid and water, dried at 110°C for 16 hours and calcined at 500°C for two hours, giving a catalyst containing 20 weight % MoO<sub>3</sub>, 4 weight % NiC and 7 weight % 3<sub>2</sub>O<sub>5</sub>. This base catalyst (30 g) was then impregnated with 12 ml of ethanolic solution containing 7.0 g ethanedithiol or 9.1 g 1,4-butanedithiol, and dried at 100°C for 16 hours, affording catalysts F<sub>1</sub> and F<sub>2</sub>, respectively.

The amounts of dithiol loaded on these catalysts were 1.5 times the theoretical amount required to convert the two metals into MoS<sub>2</sub> and NiS.

Catalysts F<sub>1</sub> and F<sub>2</sub> prepared above were used for hydrodesulphurization of KSRGO without being activated under the same conditions as in Example 1. The average rates of desulphurization are shown in Table 6.

#### Comparative Example 4

The base catalyst of Mo/Ni/P type used in Example 4 was sulphurized in the same manner as in Comparative Example 2 and used for hydrodesulphurization of KSRGO in the same way as in Example 1. The rate of desulphurization is also shown in Table 6.

TABLE 6

Catalyst	F <sub>1</sub>	F <sub>2</sub>	Sulphurized with n-BM(°)
Bivalent mercaptan	Ethanedithiol	1,4-butanedithiol	-
Rate of desulphurization (%)	94.1	90.9	73.5

The catalysts of Mo/Ni/P type containing ethanedithiol or 1,4-butanedithiol showed higher activity than the catalyst sulphurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

#### Example 5

Thirty grams of commercial catalyst (the same type as used in Example 3) was impregnated with 13.0g 2-aminoethanethiol or 20.8 g 4-aminothiophenol, and dried at 80°C for 16 hours, giving catalyst G<sub>1</sub> and G<sub>2</sub>, respectively.

The amounts of amino-substituted mercaptan loaded on these catalysts were 1.8 times the theoretical amount required to convert the two metals into MoS<sub>2</sub> and CoS.

Catalysts G<sub>1</sub> and G<sub>2</sub> prepared above were activated in the same manner as in Example 1 and used for hydrodesulphurization of KSRGO under the same conditions. The average rate of desulphurization are shown in Table 7.

#### Comparative Example 5

The base catalyst of Mo/Co type used in Example 5 was sulphurized in the same manner as in Comparative Example 1 and used for hydrodesulphurization of KSRGO in the same way as in Example 1. The rate of desulphurization is also shown in Table 7.

The catalysts of Mo/Co type containing 2-aminoethanethiol or 4-aminothiophenol showed higher activity than that sulphurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

TABLE 7

Catalyst	G <sub>1</sub>	G <sub>2</sub>	Sulphurized with n-BM(°)
Amino-substituted mercaptan	2-Aminoethanethiol	4-Aminothiophenol	-
Amount (°)	x1.8	x1.8	
Rate of desulphurization (%)	81.7	85.0	81.5

#### Example 6



One hundred grams of  $\gamma$ -alumina carrier (the same type as used in Example 2) was impregnated with 80 ml of a solution prepared from 29.0 g molybdenum trioxide, 10.5 g nickel carbonate (Ni content: 43.3%), 16.5 g of 85% phosphoric acid and water, dried at 110°C for 16 hours and calcined at 500°C for two hours, giving a base catalyst containing 20 weight %  $\text{MoC}_3$ , 4 weight % NiO and 7 weight %  $\text{P}_2\text{O}_5$ . Catalysts  $\text{H}_1$  and  $\text{H}_2$  were prepared by impregnating the base catalyst (30 g) obtained above with 30 ml of aqueous solution containing 11.5 g 2-aminoethanethiol or 18.6 g 4-aminothiophenol, drying at 100°C for 16 hours, and repeating the impregnating and drying steps once again.

The amounts of amino-substituted mercaptan loaded on these catalysts were 1.5 times the theoretical amount required to convert the two metals into  $\text{MoS}_2$  and NiS.

Catalysts  $\text{H}_1$  and  $\text{H}_2$  prepared above were used for hydrodesulphurization of KSRGO without being activated under the same conditions as in Example 1. The average rates of desulphurization are shown in Table 8.

#### Comparative Example 6

The base catalyst of Mo/Ni/P type used in Example 6 was sulphurized in the same manner as in Comparative Example 1 and used for hydrodesulphurization of KSRGO in the same way as in Example 1. The rate of desulphurization is also shown in Table 8.

Table 8

Catalyst	$\text{H}_1$	$\text{H}_2$	Sulphurized with n-BM(%)
Amino-substituted mercaptan Amount (%)	2-Aminoethanethiol x1.5	4-Aminothiophenol x1.5	-
Rate of desulphurization (%)	83.1	90.6	73.5

The catalysts of Mo/No/P type containing 2-aminoethanethiol or 4-aminothiophenol showed higher activity than the catalyst that sulphurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

#### Example 7

Thirty grams of commercial catalyst (the same type as used in Example 5) was impregnated with 15 ml of ethanolic solution containing 12.7 g thioacetic acid or 23.0 g thiobenzoic acid, and dried at 80°C for 16 hours, giving catalysts  $\text{I}_1$  and  $\text{I}_2$  respectively.

The amounts of thio-acid loaded on these catalysts were 1.8 times the theoretical amount required to convert the two metals into  $\text{MoS}_2$  and CoS.

Catalysts  $\text{I}_1$  and  $\text{I}_2$  prepared above were activated in the same manner as in Example 1 and used for hydrodesulphurization of KSRGO under the same conditions. The average rates of desulphurization are shown in Table 9.

#### Comparative Example 7

The base catalyst of Mo/Co type used in Example 5 was sulphurized in the same manner as in Comparative Example 1 and used for hydrodesulphurization of KSRGO in the same way as in Example 1. The rate of desulphurization is also shown in Table 9.

The catalysts of Mo/Co type containing thioacetic acid or thiobenzoic acid showed higher activity than that sulphurized with a maximum of 3 weight % n-butylmercaptan and KSRGO.

Table 9

Catalyst	$\text{I}_1$	$\text{I}_2$	Sulphurized with n-BM(%)
Thio-acid Amount (%)	Thioacetic acid x1.8	Thiobenzoic acid x1.8	-
Rate of desulphurization (%)	85.1	82.0	81.5

**Example 8**

One hundred grams of  $\gamma$ -alumina carrier (the same type as used in Example 2) was impregnated with 80 ml of a solution prepared from 29.0 g molybdenum trioxide, 10.5 g nickel carbonate (Ni content: 43.3%), 16.5 g of 85% phosphoric acid and water, dried at 110°C for 16 hours and calcined at 500°C for two hours, giving a catalyst containing 20 weight %  $\text{MoO}_3$ , 4 weight % NiO and 7 weight %  $\text{P}_2\text{O}_5$ . This base catalyst (30 g) was impregnated with 15 ml of ethanolic solution containing 11.3 g thioacetic acid or 20.6 g thiobenzoic acid, and dried at 110°C for 16 hours, giving catalyst  $J_1$  and  $J_2$ , respectively.

The amounts of thio-acid loaded on these catalysts were 1.5 times the theoretical amount required to convert the two metals into  $\text{MoS}_2$  and NiS.

Catalysts  $J_1$  and  $J_2$  prepared above were used for hydrodesulphurization of KSRGO without being activated under the same conditions as in Example 1. The average rates of desulphurization are shown in Table 10.

**Comparative Example 8**

The base catalyst of Mo/Ni/P type used in Example 8 was sulphurized in the same manner as in Comparative Example 1 and used for hydrodesulphurization of KSRGO in the same way as in Example 1. The rate of desulphurization is also shown in Table 10.

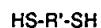
Table 10

Catalyst	$J_1$	$J_2$	Sulphurized with n-BM(*)
Thio-acid	Thioacetic acid	Thiobenzoic acid	-
Amount (**)	x1.5	x1.5	
Rate of desulphurization (%)	74.8	90.5	73.5

The catalysts of Mo/Ni/P type containing thioacetic acid or thiobenzoic acid showed higher activity than that sulphurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

**Claims**

1. A catalyst for hydrotreating hydrocarbons, the catalyst being supported on an inorganic oxide carrier and comprising: (a) at least one oxide of a metal in Periodic Table Groups VI or VIII, and (b) at least one organic compound having a mercapto radical or radicals (-SH) selected from: bivalent mercaptans represented by the following general formula:



(wherein  $\text{R}'$  is a bivalent hydrocarbonaceous radical); amino-substituted mercaptans represented by the following general formula:



(wherein  $\text{R}'$  is as defined above); and thiocarboxylic acids represented by the following general formula:



(wherein  $\text{R}''$  is a monovalent hydrocarbonaceous radical).

2. A catalyst for hydrotreating hydrocarbons according to claim 1, wherein said inorganic oxide carrier comprises at least one of alumina, silica-alumina and titania.
3. A catalyst for hydrotreating hydrocarbons according to claim 1, wherein said Group VI metal is molybdenum and/or tungsten and said Group VIII metal is cobalt and/or nickel.
4. A catalyst for hydrotreating hydrocarbons according to claim 3, wherein the catalyst also contains

phosphorus as a component element.

5. A catalyst for hydrotreating hydrocarbons according to claim 1, wherein said bivalent mercaptan is ethanedithiol ( $\text{HSCH}_2\text{CH}_2\text{SH}$ ) and/or 1, 4-butanedithiol ( $\text{HS}(\text{CH}_2)_4\text{SH}$ ).
6. A catalyst for hydrotreating hydrocarbons according to claim 1, wherein said amino-substituted mercaptan is 2-aminoethanethiol ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{SH}$ ) and/or 4-aminothiophenol ( $\text{H}_2\text{NC}_6\text{H}_4\text{SH}$ ).
7. A catalyst for hydrotreating hydrocarbons according to claim 1, wherein said thiocarboxylic acid formula,  $\text{R}''\text{-COSH}$  is thioacetic acid ( $\text{CH}_3\text{COSH}$ ) and/or thiobenzoic acid ( $\text{C}_6\text{H}_5\text{COSH}$ ).
8. A method of activating a hydrotreating catalyst for hydrocarbons according to any one of claims 1-7, the catalyst being supported on an inorganic oxide carrier, by treatment at a temperature from room temperature to  $400^\circ\text{C}$  in the presence of hydrogen gas, said catalyst comprising (a) at least one oxide of a metal in Period Table Group VI or VIII, and (b) at least one organic compound having a mercapto radical or radicals ( $-\text{SH}$ ) selected from: bivalent mercaptans represented by the following general formula:
 

$\text{HS-R}'\text{-SH}$

(wherein  $\text{R}'$  is a bivalent hydrocarbonaceous radical); amino-substituted mercaptans represented by the following general formula:

$\text{H}_2\text{N-R}'\text{-SH}$

(wherein  $\text{R}'$  is as defined above); and thiocarboxylic acids represented by the following general formula:

$\text{R}''\text{-COSH}$

(wherein  $\text{R}''$  is a monovalent hydrocarbonaceous radical).
9. A method of activating a hydrotreating catalyst for hydrocarbons according to claim 8, in which said inorganic oxide carrier comprises at least one of alumina, silica-alumina and titania.
10. A method of activating a hydrotreating catalyst for hydrocarbons according to claim 8, wherein said Group VI metal is molybdenum and/or tungsten and said Group VIII metal is cobalt and/or nickel.
11. A method of activating a hydrotreating catalyst for hydrocarbons according to claim 10, wherein said catalyst also contains phosphorus as a component element.
12. A method of activating a hydrotreating catalyst for hydrocarbons according to claim 8, wherein said bivalent mercaptan is ethanedithiol ( $\text{HSCH}_2\text{CH}_2\text{SH}$ ) and/or 1,4-butanedithiol ( $\text{HS}(\text{CH}_2)_4\text{SH}$ ).
13. A method of activating a hydrotreating catalyst for hydrocarbons according to claim 8, wherein said amino-substituted mercaptan is 2-aminoethanethiol ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{SH}$ ) and/or 4-aminothiophenol ( $\text{H}_2\text{NC}_6\text{H}_4\text{SH}$ ).
14. A method of activating a hydrotreating catalyst for hydrocarbons according to claim 8, wherein said thiocarboxylic acid is thioacetic acid ( $\text{CH}_3\text{COSH}$ ) and/or thiobenzoic acid ( $\text{C}_6\text{H}_5\text{COSH}$ ).
15. A method of activating hydrotreating catalysts for hydrocarbons according to claim 8, wherein said temperature is in the range from 100 to  $300^\circ\text{C}$ .



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# EUROPEAN SEARCH REPORT

Application Number

EP 92 20 1346

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	EP-A-0 064 429 (INSTITUT FRANCAIS DU PETROLE) * claims 1-4 * * example 1 * ---	1-3, 8-10	801J37/20 C10G45/08
Y	US-A-3 531 545 (J. GARNIER) * column 3, line 73 - column 4, line 20 * ---	1-3, 8-10	
A	GB-A-1 575 434 (GULF RESEARCH) * claims 1,2 * ---		
A	EP-A-0 181 254 (EURECAT) ---		
A	US-A-4 636 487 (S. PAROTT) ---		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			801J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30 JULY 1992	Examiner THION M.A.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document			

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